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EFFECT OF GAMMA RADIATION ON THE PROPERTIES OF BISMUTH-CONTAINING GLASSES AND GLASS CERAMICS

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Glasses and glass ceramic materials with the compositions (in moles) $2\text{Bi}_2\text{O}_3$; 3SiO_2 and $2\text{Bi}_2\text{O}_3$; 3GeO_2 were irradiated with γ -rays at doses 10^5 and 10^6 rad. The pre- and post-irradiation absorption spectra, microhardness and refractive indices of the glass and glass ceramic samples were studied. It was shown that gamma radiation gives rise to ionization of the bismuth ions and crystallization of the glasses. The bismuth-silicate glass ceramic was less affected less by γ -radiation than the bismuth-germanate ceramic.

Key words: radiation resistance, γ -radiation, bismuth-containing glasses and glass ceramic.

Eulytin ($\text{Bi}_4\text{Si}_3\text{O}_{12}$ and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$) single crystals have high radiation resistance and good scintillation properties, as a result of which they are widely used in high-energy radiation experiments [1] and, when doped with rare-earth ions, as laser materials [2].

For applications of glass and glass ceramic bismuth germanates and silicates as scintillation materials it is necessary to study the effect of γ -radiation on the following glass compositions (in moles): $2\text{Bi}_2\text{O}_3$; 3SiO_2 and $2\text{Bi}_2\text{O}_3$; 3GeO_2 and glass ceramic materials based on these glasses.

A phase with eulytin structure crystallizes in the systems Bi_2O_3 – SiO_2 and Bi_2O_3 – GeO_2 with the components taken in the ratio 2 : 3. Single crystals of eulytin $\text{Bi}_4\text{Si}_3\text{O}_{12}$ and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ are used to detect high-energy electromagnetic radiation (x- and γ -rays) [1, 3]. The applications of such radiation detectors range from high-energy physics to radiological and radioecological assaying [4], for example, checking the fuel elements of nuclear reactors [5].

Bismuth germanate $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ has a number of advantages over other scintillation materials. The main ones are high density and short radiation length, which permit making small-size detectors having the same operating efficiency [3, 5]. Other advantages are non-hygroscopicity and good

mechanical properties during working. $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ exhibits high radiation resistance compared with other inorganic scintillators, and its radiation resistance depends on the crystal dimensions, impurities and production methods [3].

Bismuth silicate $\text{Bi}_4\text{Si}_3\text{O}_{12}$ crystals can be used as a faster scintillation material, but there are advantages and disadvantages over germanium silicate [1]. The advantages are as follows: lower cost of production because of the low cost of the initial materials; higher radiation resistance, which permits using this material in high-energy experiments; and, shorter persistence time. A drawback is that its maximum light output is only 20% of the Ge-eulytin value.

At the same time it is known [6] that when bismuth oxide interacts with glass-forming oxides, including SiO_2 and GeO_2 , bismuth-containing glasses form with the same ratios of the initial components as eulytin crystals. Glasses are technologically more workable and less expensive to manufacture.

Such glasses have found application in Raman spectroscopy [6], and because their electric conductivity is strongly temperature dependent [7] they hold promise for use in cryogenic sensors. In addition, bismuth-containing glasses are attracting attention because of their scintillation properties and quite high radiation resistance [8], which is nonetheless an order of magnitude lower than that of single crystals, while the persistence time for glasses is longer.

One way to improve glass characteristics (bringing glasses closer to single crystals) is to obtain pyroceramic or glass ceramic material containing a quite large amount (at least 50 vol.%) of the required crystalline phase. If the dimensions

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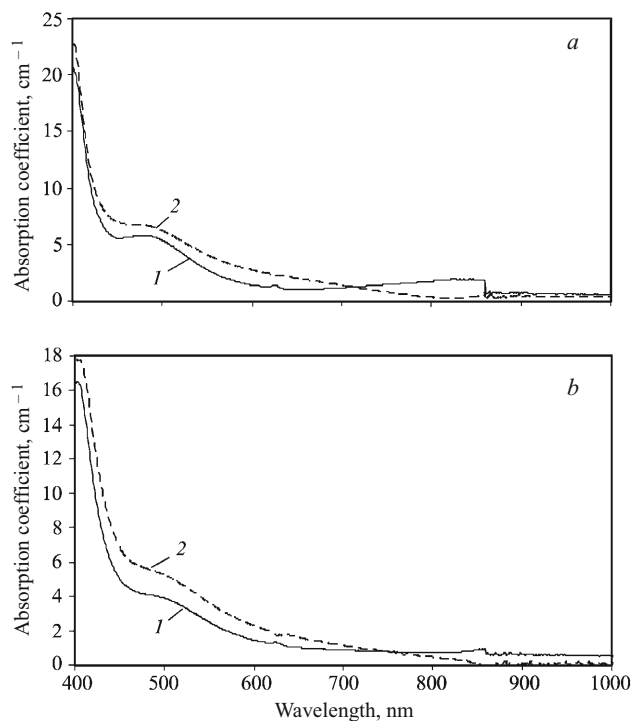


Fig. 1. The absorption spectra of glasses before (1) and after (2) irradiation to dose 10^5 rad: a) $2\text{Bi}_2\text{O}_3$; 3SiO_2 (in moles); b) $2\text{Bi}_2\text{O}_3$; 3GeO_2 (in moles).

of the crystallites do not exceed 300 nm, such a material remains transparent, just as the initial glass. However, in this case the characteristics of the material are close to those of single crystals.

In the present work glass was obtained by the standard method of pouring melt onto a platinum substrate. The glasses were crystallized by heat-treatment at temperatures corresponding to the crystallization temperatures determined by the dilatometric method. For glass ceramic material with the composition (in moles) $2\text{Bi}_2\text{O}_3$; 3SiO_2 the volume fraction of the crystal phase was $> 50\%$, and the approximate sizes of the crystallites were 50 nm, while for the composition (in moles) $2\text{Bi}_2\text{O}_3$; $3\text{Ge}_2\text{O}_3$ the volume fraction of the crystal phase was $> 70\%$ and the approximate sizes were 30 nm.

To determine the radiation resistance glasses and glass ceramics with both compositions were irradiated with γ -rays (^{60}Co source, 10^5 and 10^6 rad).

After irradiation the color of the glasses was practically unchanged and the glass ceramic samples are darker. Over a period of 14 days following irradiation the glass ceramic material returns to its initial color while the glasses do not show any visible color changes.

The absorption spectra of the glasses and glass ceramic materials exposed to irradiation dose 10^5 rad are shown in Figs. 1 and 2, where they are compared with the absorption spectra of the unirradiated glasses and glass ceramic materi-

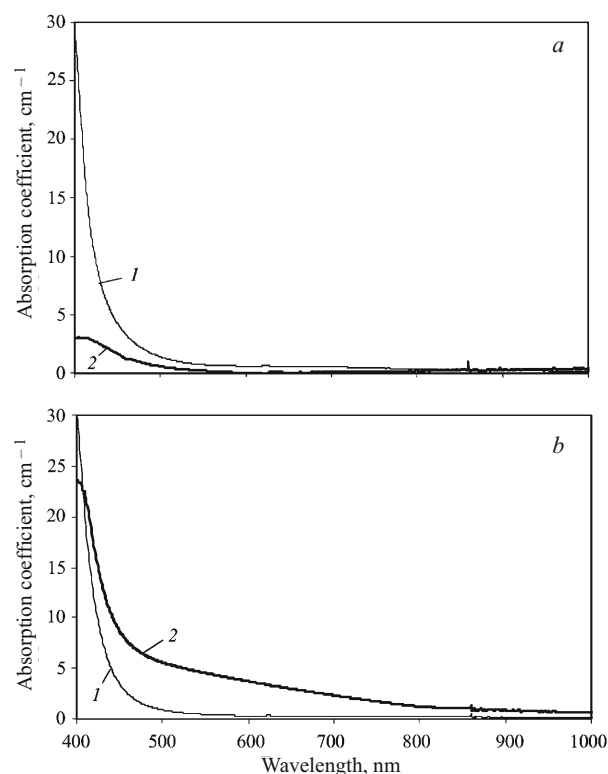


Fig. 2. The absorption spectra of glass ceramics before (1) and after (2) irradiation to dose 10^5 rad: a) $2\text{Bi}_2\text{O}_3$; 3SiO_2 (in moles); b) $2\text{Bi}_2\text{O}_3$; 3GeO_2 (in moles).

als. The post-irradiation absorption in glasses is higher at short wavelengths and lower at longer wavelengths.

A small absorption band appears in the region 450–500 nm of the absorption spectra of the irradiated glass ceramic with the composition (in moles) $2\text{Bi}_2\text{O}_3$; 3SiO_2 . For the irradiated glass ceramic with the composition (in moles) $2\text{Bi}_2\text{O}_3$; 3GeO_2 this band is wider while the absorption increases practically in the entire visible range.

The darkening of the samples exposed to γ -rays is probably due to the ionizing action of the radiation and the formation of color centers due to the appearance of free electrons and holes. Specifically, it can be said that this process is similar to the oxidation of bismuth, i.e., Bi^{4+} (Bi^{5+}) forms as a result of electron detachment from the outer shell of the Bi^{3+} ion. The color change of the glass ceramic material is probably due to this process, and the absorption bands appearing in the spectra in the short wavelength region of the spectrum are due to precisely the presence of bismuth with a higher degree of oxidation. With time (two weeks) after irradiation electron–hole recombination occurs and the previous color is restored.

However, γ -rays can initiate crystallization in glass, as a result of which the ionization of bismuth ions either does not occur at all or is much weaker, as a result of which there are no visually noticeable color changes. The color of the glasses

TABLE 1. Variation of the Refractive Index of Glasses and Glass Ceramic Materials Irradiated with γ -Rays

Indicator	Refractive index, arb. units, sample composition (in moles)			
	2Bi ₂ O ₃ ; 3SiO ₂		2Bi ₂ O ₃ ; 3GeO ₂	
	Glass	Glass ceramic material	Glass	Glass ceramic material
Before irradiation	1.83 ± 0.01	1.98 ± 0.01	1.90 ± 0.01	2.09 ± 0.01
Irradiation 10 ⁵ rad	1.85 ± 0.01	1.95 ± 0.01	1.96 ± 0.01	2.05 ± 0.01
Irradiation 10 ⁶ rad	1.85 ± 0.01	1.94 ± 0.01	1.97 ± 0.01	2.05 ± 0.01
After 14 days (10 ⁶ rad)	1.85 ± 0.01	1.96 ± 0.01	1.97 ± 0.01	2.08 ± 0.01

TABLE 2. Variation of the Microhardness of Glasses and Glass Ceramic Material Irradiated with γ -Rays

Indicator	Microhardness, 10 ⁷ Pa, samples with composition (in moles)			
	2Bi ₂ O ₃ ; 3SiO ₂		2Bi ₂ O ₃ ; 3GeO ₂	
	Glass	Glass ceramic material	Glass	Glass ceramic material
Before irradiation	188 ± 13	206 ± 15	156 ± 12	165 ± 12
Irradiation 10 ⁵ rad	190 ± 13	193 ± 14	152 ± 12	156 ± 12
Irradiation 10 ⁶ rad	202 ± 15	186 ± 14	167 ± 12	150 ± 14
After 14 days (10 ⁶ rad)	182 ± 13	190 ± 14	150 ± 12	170 ± 13

remains unchanged fourteen days after irradiation, since irradiation-induced crystallization is an irreversible process. For glasses and glass ceramic material both processes can occur, and the dominant process determines the color and other characteristics.

The values of the microhardness and refractive indices of the irradiated glasses and glass ceramic materials with both compositions are presented in Tables 1 and 2.

As the irradiation dose increases the refractive indices and microhardness of the glasses increase. This could be due to crystallization, while in the glass ceramic materials they decrease as a result of the formation of defects in the crystal lattice.

Fourteen days after irradiation the values of the refractive indices of the glass ceramic materials return to the pre-irradiation values (see Table 1). The microhardness changes to pre-irradiation values in almost all cases (Table 1). This shows that γ -radiation has a large effect on the structure of the glasses and glass ceramic materials but with time the effect becomes weaker or vanishes as a result of partial or complete recombination of the defects formed in the material.

The changes occurring in the germanate glasses and especially in the glass ceramic are greater than in silicate glasses and glass ceramic (stronger post-irradiation absorption, larger change of the refractive index and microhardness after irradiation), which correlates with the data [4] obtained for bismuth silicate germanate single crystals, indicating that

bismuth-silicates are more radiation-resistant than bismuth-germanates.

CONCLUSIONS

1. Gamma radiation acts differently on glass and glass ceramic material:

- glass color remains practically unchanged;
- glass ceramic darkens appreciably;
- the refractive indices and microhardness increase in glasses and decrease in glass ceramic materials.

2. Fourteen days after irradiation:

- the characteristics of the glass ceramic samples are practically completely restored, as are the characteristics of eulytin single crystals;
- the color and refractive index of glasses do not change appreciably over 14 days.

3. All observed effects are due to the fact that under gamma irradiation ionization of bismuth ions and crystallization of glass occur simultaneously. Crystallization predominates in glass and ionization in glass ceramic.

4. Bismuth-silicate glass ceramic is less affected by γ -radiation than bismuth-germanate glass ceramic.

REFERENCES

1. M. Ishii, K. Harada, Y. Hirose and X. Q. Feng, "Development of BSO (Bi₄Si₃O₁₂) crystal for radiation detector," *Opt. Mater.*, **19**, 201 – 212 (2002).

2. A. A. Kaminskii, N. V. Kravtsov, N. I. Naumkin, et al., "Polarization magneto-optical effects in a $\text{Nd}^{3+}:\text{Bi}_4\text{Ge}_3\text{O}_{12}$ continuous-wave laser ($\lambda = 1.06425$ and $1.3418\ \mu\text{m}$) with semiconductor pumping," *Kvant. Élektron.*, **30**(4), 283 – 284 (2000).
3. Yu. K. Akimov, "Nuclear-radiation detectors based on inorganic scintillators," *Fiz. Élement. Chastits At. Yadra*, **25**(1), 229 – 284 (1994).
4. S. F. Burachas, L. L. Nagornaya, G. M. Onishchenko, et al., "Advanced scintillation single crystals based on complex oxides with large atomic number," *Semiconductor Physics. Quantum Electronics & Optoelectronics*, **3**(2), 237 – 239 (2000).
5. S. E. Derenzo, M. J. Weber, E. Bourret-Courchesne, and M. K. Klintenberg, "The quest for the ideal inorganic scintillator," *Nucl. Instr. Meth. Phys. Res. A*, **505**, 111 – 117 (2003).
6. P. Beneventi, D. Bersani, P. P. Lottici, et al., "Raman study of $\text{Bi}_2\text{O}_3\text{--GeO}_2\text{--SiO}_2$ glasses," *J. Non-Cryst. Solids*, **192 – 193**, 258 – 262 (1995).
7. B. Kusz and K. Trezebiatowski, "Bismuth germanate and bismuth silicate glasses in cryogenic detectors," *J. Non-Cryst. Solids*, **319**, 257 – 262 (2003).
8. B. Kelly, *Irradiation Damage to Solids* [Russian translation], Moscow (1970).